Physical Aging of Ultrathin Polymer Films above and below the Bulk Glass Transition Temperature: Effects of Attractive vs Neutral Polymer−Substrate Interactions Measured by Fluorescence

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Received September 28, 2004
Revised Manuscript Received December 10, 2004

Introduction. Nanoscopically confined polymers and low molecular weight glass-formers often exhibit a deviation in glass transition temperature (T_g) from that of the bulk material.[1−18] With confined, supported films, there is evidence that a depression in T_g is due to enhanced mobility near the air−polymer surface[5−11,13] while an increase in T_g is associated with attractive polymer−substrate interactions[3,8,10,14,15,18,19] that may overwhelm the free-surface effects.[11,15,18]

Potentially of equal scientific and technological importance as the T_g is the physical aging of nanoconfined glasses.[10] In the case of polymers, physical aging is the structural relaxation below T_g of the chains from their nonequilibrium conformations to an overall conformational state at equilibrium. With bulk systems, this leads to time-dependent properties including increases in density, modulus, and yield stress and decreases in specific enthalpy, impact strength, fracture energy, and ultimate elongation.[20,21] Unlike the many T_g nanoconfinement studies, there are few reports on physical aging of confined glasses.[10,22−24] Kawana and Jones[22] used ellipsometry to study polystyrene (PS) supported on silicon; at 30 K below the bulk glass transition temperature ($T_{g,bulk}$), an 18 nm thick film exhibited aging while a 10 nm thick film did not. Lu and Nutt[23] reported reduced enthalpy relaxation for epoxy−clay nanocomposites compared to that of neat epoxy. In contrast, Simon et al.[24] reported that the enthalpy relaxation of a low molecular weight glass-former confined to nanopores was faster than in bulk due to the combined effects of isochoric aging and the fact that confinement had reduced the T_g.

Here we provide the first characterization of physical aging as a function of polymer−substrate interactions, attractive in the case of poly(methyl methacrylate) (PMMA)/silica substrate films and nonattractive in the case of PS/silica substrate films, in nanoconfined polymers. We employ fluorescence of mobility-sensitive or free-volume-sensitive chromophores, similar to methods used to characterize aging in bulk polymer.[25−30] These chromophores exhibit an increase in fluorescence with a decrease in local mobility or free volume, which accompanies densification during aging. Royal and Torkelson[28] found that the temperature dependence of the physical aging rate measured by julolidine malononitrile (JMN) doped in a variety of polymers agreed qualitatively with the temperature dependence of the rate of volume relaxation.[31] Using 4-tricyanovinyl-[*N*-(2-hydroxyethyl)-*N*-ethyl]aniline (TC1), with a higher quantum yield than JMN,[32] Ellison et al.[10] extended this approach to monitor aging at $T_{g,bulk}$ − 25 K in ultrathin poly(isobutyl methacrylate) (PIBMA) films supported on silica. They found that the aging rate was roughly independent of thickness down to 10 nm. In the present study, we employ TC1 as a dopant (in a simple mixture with PS, without covalent attachment to the polymer)[33] or as a label covalently attached at trace levels to PMMA.[34] Using thin (500 nm thick) and ultrathin (20 nm thick) PS and PMMA films supported on silica, we demonstrate that aging in confined systems can be suppressed at temperatures below $T_{g,bulk}$ or induced at temperatures above $T_{g,bulk}$, depending on the level of attractive polymer−substrate interactions. We also show how confinement can affect the temperature dependence of the aging rate below $T_{g,bulk}$.

Experimental Section. Polystyrene was synthesized by free radical polymerization (FRP): M_n = 354 000 g/mol, M_w/M_n = 1.76 by gel permeation chromatography (GPC) relative to PS standards; $T_{g,onset}$ = 376 K[35] (DSC, 10 K/min heating rate, second heating). Poly(methyl methacrylate) was synthesized by FRP: M_n = 355 000 g/mol, M_w/M_n = 1.54, by GPC universal calibration;[36] $T_{g,onset}$ = 394 K.[35] The probe TC1 was synthesized using procedures in refs 37 and 38. Following ref 39, PMMA was synthesized incorporating a trace of TC1-labeled methacrylate monomer: M_n = 150 000 g/mol, M_w/M_n = 1.60, by GPC universal calibration;[36] $T_{g,onset}$ = 393 K;[35] 0.24 mol % TC1 label (UV−vis absorbance). Polymers were thoroughly washed and dried[40] prior to use.

Films were spin-cast from toluene solutions onto quartz slides.[41] Doped films contained less than 0.50 wt % TC1; labeled PMMA films contained 0.24 mol % TC1. Films were dried under vacuum at $T_{g,bulk}$ + 5 K for 8 h. Thickness was measured by profilometry, taking the average of at least four measurements. Prior to each aging experiment, the thermal history was erased by annealing at $T_{g,bulk}$ + 25 K for 20 min. Films were quenched using a temperature-controlled cell holder preset to the aging temperature. Fluorescence was recorded using a Photon Technology International fluorimeter in front-face geometry with 3.0 mm excitation and emission slits (12.0 nm band-pass) and a 480 nm excitation wavelength. Physical aging was monitored by measuring the maximum intensity (at 550−555 nm for TC1-doped PS and at 560−565 nm for TC1-labeled PMMA).

Results and Discussion. Figure 1 shows the emission spectrum of a 500 nm thick, TC1-labeled PMMA film. After absorption of light and promotion of an electron to an excited singlet state, TC1 returns to the ground state by internal conversion (energy loss by vibrational and rotor motions) or by fluorescence. The film densifies upon aging, suppressing internal conversion and yielding an increase in fluorescence intensity.[42] The 38% increase in intensity over 460 min of physical aging at 305 K ($T_{g,bulk}$ − 88 K) exceeds that observed in various JMN-doped polymers[27,28] as well as in TC1-labeled PIBMA.[10] By comparison, TC1-doped PMMA yields a 6−7% increase in intensity at the same conditions[43] used in Figure 1.

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10.1021/ma047994o CCC: $30.25
Published on Web 01/11/2005

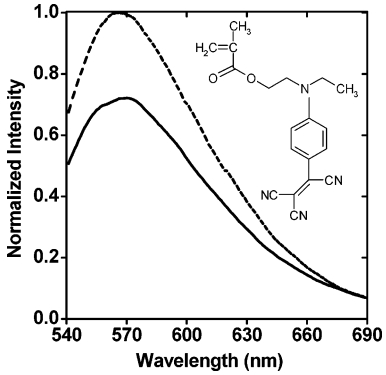

Figure 1. Fluorescence emission spectrum of a 500 nm thick TC1-labeled PMMA film as a function of physical aging time after a temperature jump from above $T_{g,bulk}$ to $T_{g,bulk}$ − 88 K: 10 min (solid line); 460 min (dashed line). Inset: molecular structure of TC1-labeled methacrylate monomer used in the labeling procedure.

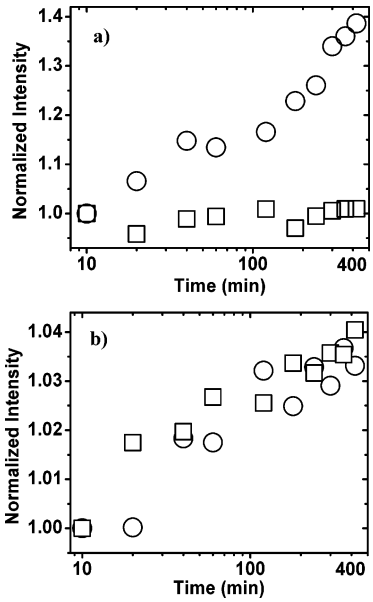

Figure 2. (a) Normalized fluorescence intensity of a 500 nm thick TC1-labeled PMMA film as a function of logarithmic aging (or annealing) time after quenching from $T_{g,bulk}$ + 25 K to the following temperature: $T_{g,bulk}$ − 88 K (305 K) (circles); $T_{g,bulk}$ + 7 K (400 K) (squares). The invariance of intensity with annealing time at $T_{g,bulk}$ + 7 K indicates that the polymer is at equilibrium. (b) Normalized fluorescence intensity of a 20 nm thick TC1-labeled PMMA film as a function of logarithmic aging or annealing time after quenching from $T_{g,bulk}$ + 25 K to the following temperature: $T_{g,bulk}$ − 88 K (circles); $T_{g,bulk}$ + 7 K (squares). The TC1 label is able to monitor aging in the ultrathin film at $T_{g,bulk}$ + 7 K, indicating that the ultrathin film is not at equilibrium.

Figure 2 compares the effects of aging temperature and nanoconfinement on the physical aging of TC1-labeled PMMA. Intensities are normalized at 10 min after quenching from well above $T_{g,bulk}$ to ensure that thermal equilibrium had been achieved in the films annealed at $T_{g,bulk}$ + 7 K as well as those annealed at $T_{g,bulk}$ − 88 K. When the 500 nm thick film is aged below $T_{g,bulk}$, there is a roughly linear increase in intensity with logarithmic aging time, similar to aging monitored by enthalpy recovery[27] and density.[20,31,42] When the thin film is aged above $T_{g,bulk}$, there is no increase in intensity, consistent with the film being at equilibrium.

In contrast to the thin film, the ultrathin film exhibits a much smaller, 4% increase in intensity over 460 min

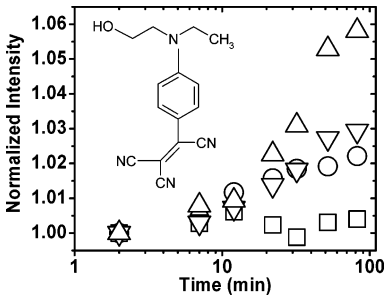

Figure 3. Normalized fluorescence intensity as a function of logarithmic aging or annealing time for 500 nm thick TC1-doped PS films at $T_{g,bulk}$ − 10 K (366 K) (triangles up) and $T_{g,bulk}$ − 71 K (305 K) (triangles down) and for 20 nm thick TC1-doped PS films at $T_{g,bulk}$ − 10 K (366 K) (squares) and $T_{g,bulk}$ − 71 K (305 K) (circles). Physical aging was initiated by a temperature jump from $T_{g,bulk}$ + 25 K to the temperature of interest. The invariance of intensity with annealing time for the 20 nm thick film at $T_{g,bulk}$ − 10 K indicates that the polymer is at equilibrium. Inset: molecular structure of TC1. (Note: Over the entire aging time the probes response to aging is not completely logarithmic. At very early aging times there appears to be an initial plateau in the aging response. Similar physical aging responses have been observed previously in bulk PS samples studied by fluorescence or volumetric relaxation.[28,31])

of aging at $T_{g,bulk}$ − 88 K. Furthermore, unlike the 500 nm thick film, the 20 nm thick film exhibits aging when annealed at $T_{g,bulk}$ + 7 K, a clear indication that the ultrathin film in not at equilibrium. Several factors may contribute to these effects. First, as a result of attractive PMMA−substrate interactions, the ultrathin film has a T_g that exceeds $T_{g,bulk}$,[14] thereby allowing for aging at temperatures above $T_{g,bulk}$. Evidence for the enhanced T_g is obtained from a break in the temperature (T) dependence of the fluorescence intensity of the ultrathin film of TC1-labeled PMMA at 407 K or $T_{g,bulk}$ + 14 K; in contrast, the 500 nm thick TC1-labeled PMMA exhibited a break in the T dependence of fluorescence intensity at 393 K, exactly the value of $T_{g,bulk}$ for this sample. Previous studies[10,11,15,18] have shown that the break in the T dependence of the fluorescence of a trace amount of pyrene probe or label yields accurate T_g values in both bulk and nanoconfined polymer films. For further discussion, see ref 44. This also means that the thin and ultrathin films aged deep in the glassy state at 305 K have been aged at different temperatures relative to their own T_g values; physical aging is known to depend on quench depth below T_g.[21,28,31] Second, it is postulated that attractive polymer−substrate interactions may significantly retard structural relaxation in ultrathin films.[45] A final potential contributing factor may be related to the effect of confinement on the sub-T_g β-relaxation, which has long been understood to be correlated with the presence of physical aging.[46] At present, there are several reports[17,47,48] regarding the impact of nanoconfinement on the β-relaxation of PMMA. However, because of differences in sample tacticity and substrate interaction, there is not a consensus among these reports on the effect of nanoconfinement on the β-relaxation. Further study of this issue and its correlation with physical aging in confined polymers is warranted.

Figure 3 compares the effects of temperature and nanoconfinement on physical aging of TC1-doped PS[49] over an 80 min aging time. In agreement with previous studies of bulk PS,[26,31] the 500 nm thick film ages faster at $T_{g,bulk}$ − 10 K than at $T_{g,bulk}$ − 71 K. At $T_{g,bulk}$ − 71

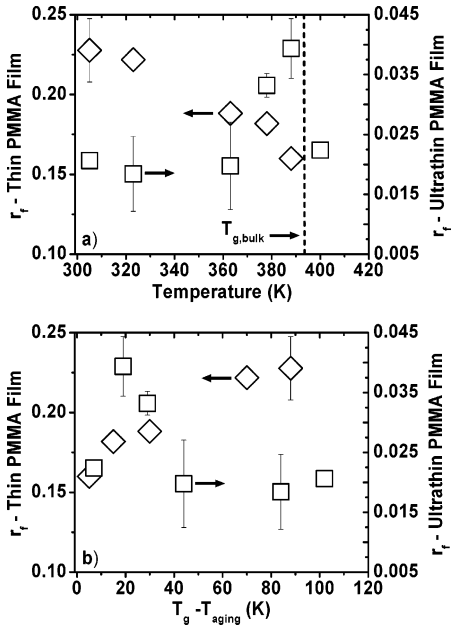

Figure 4. (a) Fluorescence aging rate, r_f, as a function of physical aging temperature for thin (500 nm thick) (diamonds) and ultrathin (20 nm thick) (squares) TC1-labeled PMMA films. (b) Fluorescence aging rate, r_f, as a function of aging quench depth below T_g for thin (500 nm thick) (diamonds) and ultrathin (20 nm thick) (squares) TC1-labeled PMMA films. (Fluorescence aging rate is calculated using eq 1 and evaluating data similar to those in Figure 2 over a physical aging time scale ranging from 10 to 460 min.) See ref 51 for details of reproducibility of aging rates and error analysis.

K, the 20 nm thick PS film exhibits about the same aging as the 500 nm thick PS film. However, when annealed at $T_{g,bulk} - 10$ K, the ultrathin film exhibits, within error, no aging. This evidence of structural equilibrium in a PS ultrathin film below $T_{g,bulk}$ agrees with findings by Kawana and Jones,[22] who observed no structural relaxation in a 10 nm thick PS film aged at $T_{g,bulk} - 30$ K. The absence of physical aging in nanoconfined PS films at a temperature below $T_{g,bulk}$ may be explained by the fact that such films exhibit strong T_g depressions. Data by Ellison et al.[10,11,15] and Keddie et al.[2] indicate that a 20 nm thick PS film exhibits a T_g that is depressed by 14−17 K relative to $T_{g,bulk}$; extrapolations of the same data suggest that a 10 nm thick PS film has a T_g depressed by much more than 30 K relative to $T_{g,bulk}$.[50]

Figure 4 compares the effect of aging temperature on the "fluorescence aging rate", r_f, in thin and ultrathin PMMA films; Figure 4a does so as a function of absolute aging temperature whereas Figure 4b does so as a function of $T_g - T_{aging}$ (this is the quench depth below T_g). By analogy to specific volume aging rate,[21,31] r_f is defined as[10,28]

$$r_f = (1/F_0)(dF/d \log t_a) \quad (1)$$

where F (F_0) is fluorescence intensity at aging time t_a (at the assumed start of aging). Over the temperature range and aging time studied, the aging rate of the 500 nm thick PMMA film exhibits a maximum near 305−320 K (∼73−88 K below T_g of the 500 nm thick film) and decreases with increasing temperature approaching $T_{g,bulk}$. This is in reasonable agreement with the specific volume aging rate of bulk PMMA[31] and characterization of r_f of bulk PMMA using JMN.[28] The aging rate changes dramatically in two ways when PMMA is confined in the 20 nm thick film. First, below $T_{g,bulk}$, r_f is reduced dramatically relative to the 500 nm thick film. Second, the maximum in r_f is observed near 388 K (∼19 K below T_g of the 20 nm thick film) and is more than a factor of 2 higher than the r_f values at 320−365 K.[51] The vastly reduced aging rate in the ultrathin film may be rationalized by polymer−substrate interactions reducing the rate of structural relaxation. A postulate for the increase in aging rate with increasing temperature from 363 to 388 K in the 20 nm thick film is that the thermal energy at higher temperature may overcome some of the polymer−substrate interactions, enhancing the structural recovery. Figure 4b shows that the differences in physical aging rate observed in the 500 nm thick and 20 nm thick films cannot be ascribed to differences in T_g with film thickness. Obviously, the maximum aging rate is observed to occur much closer to T_g in the ultrathin film, and at no value of $T_g - T_{aging}$ does the aging rate of the ultrathin film approach or exceed that of the thin film. Further study of the complex roles of polymer−substrate interactions and free-surface effects on physical aging of nanoconfined polymers is underway.

Acknowledgment. This work was supported by the NSF-MRSEC program at Northwestern University (Grant DMR-0076097), a GEM Fellowship (to R.D.P.), and Northwestern University. We thank Christopher Ellison for helpful discussions.

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(33) The dopants or labels are used at concentrations that eliminate the chance for significant phase separation of segregation/aggregation. In the case of the TC1 dye system, dye aggregation can be observed by a change in the fluorescence excitation and emission spectra. The concentrations of TC1 probes or labels employed in our current study are below the concentrations at which aggregation is evident. The dyes are also used at sufficiently low concentration so that the excitation of dyes occurs evenly across the film thickness. (See: Miller, K. E.; Krueger, R. H.; Torkelson, J. M. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *35*, 2343−2349.) Other researchers (White, C.; Wu, W. L.; Pu, Y. X.; Rafailovich, M.; Sokolov, J. *Polym. Eng. Sci.* **2003**, *43*, 1241−1249) recently demonstrated that probes in polymer films do not segregate to the interfaces of such films, indicating that the dyes remain distributed across the thickness of the film.
(34) The fluorescence intensities provide direct information regarding the behavior of the polymer near the probe or label. Previous studies by our group have shown that fluorescence probe studies provide measures of both physical aging behavior (T-dependence and time to achieve equilibrium behavior) and complex relaxation phenomena (asymmetry and memory effects) that agree well with specific volume or enthalpy relaxation measurements from bulk samples that were done without probes or labels. Hence, we believe that the probe measurements described in the current study reflect the inherent relaxation behavior that would be present without probes or labels.
(35) We have taken $T_{g,bulk}$ to be equivalent to $T_{g,onset}$ because previous studies (refs 10, 11, 15, 27, 28) have shown that the T_g values determined by fluorescence correspond somewhat more closely to $T_{g,onset}$ than to $T_g(^1/_2\Delta C_p)$.
(36) The Mark−Houwink parameters at 30 °C are as follows: PS: $a = 0.716$ and $K = 0.000\ 114$ dL/g (Hutchinson, R. A.; Beurermann, S.; Paquet, D. A. *Macromolecules* **1997**, *30*, 3490−3493); PMMA: $a = 0.731$ and $K = 0.000\ 075\ 6$ dL/g (Chen, Y. J.; Li, J. B.; Hadjichristidis, N.; Mays, J. W. *Polym. Bull. (Berlin)* **1993**, *30*, 575−578).
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(40) Polymer was recovered by precipitating in methanol and redissolving in toluene to remove residual monomer. Samples were reprecipitated and redissolved a minimum of five times. Using fluorescence-detection GPC, it was found that within error all unreacted TC1-labeled monomer had been removed from the TC1-labeled PMMA. Polymers were dried under vacuum at $T_{g,bulk}$ + 15 K for 24 h.
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(42) It has been shown previously[27−30] that dyes similar to TC1 exhibit increases in fluorescence intensity during physical aging of bulk polymers in which they are incorporated. Furthermore, as viewed in plots in which the *x*-coordinate is logarithmic time, there is some correlation between the rate of change in intensity and the rate of change in specific volume,[28] some correlation between the times to achieve equilibrium in systems aged slightly below T_g as quantified by fluorescence and by enthalpy relaxation,[27] and some correlation between complex relaxation behavior observed by fluorescence and by volume relaxation.[27] These results do not imply that there is exactly a linear relationship between fluorescence changes with physical aging and either specific volume or enthalpy relaxation. However, "rotor" dyes have a strong sensitivity to local density in systems near T_g caused by the suppression of motion of the side groups off the ring structure with increasing density; the suppression of the motion of these groups reduces the rate of nonradiative decay of the excited-state dye, which then leads to an increase in fluorescence. Hence, the "rotor" dyes are well designed to provide sensitivity to physical aging.
(43) When TC1 is used as a label instead of a dopant, its quantum yield increases as a result of the more restricted mobility associated with covalent attachment. We postulate that this plays a role in the TC1-labeled PMMA exhibiting a high sensitivity to physical aging.
(44) There are some similarities and differences between the signatures of T_g provided by the T dependence of the fluorescence intensities (taken upon cooling from above T_g) of pyrene dopants/labels and TC1 dopants/labels. With both fluorescence dye systems there is a linear increase in intensity with decreasing T in the rubbery state and a second linear increase in intensity (of different slope) with decreasing T; the intersection of the two linear T dependences correlates with T_g. In the case of the pyrene probes/labels the absolute magnitude of the slope is greater above T_g than below T_g; however, for the TC1 probes/labels the magnitude of the slope is greater below T_g than above T_g. This difference may have its origin in the various mobile side groups associated with the TC1 structure that cause the dye to be known as a "rotor" probe. The suppression of the rotational motion of these side groups by increasing local density with decreasing T may yield a greater magnitude of slope in the glassy state.
(45) Hydrogen-bonding interactions between the ester side groups of PMMA and the hydroxyl groups that are normally found at the surface of glass slides should reduce conformational relaxation processes that are associated with physical aging. This interfacial effect may result in measurable differences in ultrathin films from the behavior observed in a 500 nm thick film.
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(50) The data from our various PS studies[10,11,15,18] are also in agreement with ref 2, most notably a most recent investigation (ref 18) in which we have found a strong similarity in the T_g nanoconfinement effect for six different PS samples ranging in MW from 5000 to 3 000 000 g/mol. In that investigation, we show that four PS films with thicknesses of 13−14 nm exhibited T_g reductions exceeding 30 K relative to $T_{g,bulk}$. Hence, it is reasonable to argue that a 10 nm thick PS film will exhibit a T_g that is depressed from $T_{g,bulk}$ by more than 30 K.
(51) In the case of the 20 nm thick PMMA films, the data at 305, 363, 378, and 400 K are the averages of two measurements while the data at 323 and 388 K are the averages of three measurements. In the case of the 500 nm thick PMMA film, the data point at 305 K is the average of three measurements, the data point at 323 K is the average of two measurements, and the other data are from one measurement each. Since the 500 nm thick PMMA film exhibits a T-dependent aging rate similar to that observed in a previous fluorescence study[28] multiple measurements for the 500 nm thick were only taken in the T range of maximum aging. Error bars represent the standard deviation of the measurements, and in numerous cases the symbol size is larger than the error bar.

MA047994O